Lipid Oxidation and Quality Parameters of Sausages Marketed Locally in the Town of São Paulo (Brazil)

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Abstract


Lipid oxidation constitutes one of the most important causes of the chemical deterioration of foods, especially meats. Many harmful effects on human health are associated with lipid oxidation. During a period of six weeks, samples were bought at random on city hall food markets (CHFMs) and were analysed for lipid oxidation (TBARS-test) and some quality factors – redox potential (Eh), pH and water activity (aw). The mean of Eh was X ± σn–1 = 39.03 ± 26.30 mV, ranging from –86.00 to 92.00 mV. pH mean value was X ± σn–1 = 5.97 ± 0.27, ranging from 5.08 to 6.48. Comparing the CHFMs, no statistically significant differences were observed between them in respect to pH, Eh, and aw values. TBARS mean value was X ± σn–1 = 0.44 ± 0.23 mg/kg, ranging from 0.38 ± 0.19 mg/kg (CHFM-6) to 0.58 ± 0.31 mg/kg (CHFM-2), with extreme values of 0.22 mg/kg and 1.08 mg/kg. No statistically significant correlations between TBA test values and all tested variables were detected. According to the sensorial analysis criteria of GREENE and CUMUZE (1981), 16.67% of sausage samples could be rejected and 11.11% revealed critical TBARS values.

Keywords: lipid oxidation; sausages, meat; food market; quality factors

Abbreviations: aw = water activity; CHFMs = City Hall Food Markets; Eh = redox potential; MDA = malonaldehyde; SP = State of São Paulo; TBARS = thiobarbituric-acid reactive substances

Sausages are the most important meat product consumed by the Brazilian population, contributing 1.7% to the total energy intake (MONTEIRO et al. 2000). In 1986, Brazilian industry produced about 25 000 tons of sausages. In 1993, 55 000 t were produced, and 45 000 t in the state of São Paulo alone (ANONYMOUS 1994; GONÇALVES 1995; SILVA 1995). Between 1994 and 1995, there was a 45% increase in the sausage production (SILVA 1995).

There are many factors that interfere with the food quality. Ingredients, food manufacturing, errors or prohibited alterations in the composition, a high concentration of mechanically deboned poultry meat, wrong marketing practices and poor refrigeration constitute some of these factors (PEARSON et al. 1977; HSU et al. 1977; DAWSON & GARTNER 1983; DONNELLY & ROBINSON 1995; FERRARI & TORRES 2000a, b).

The association of these factors with other problems that produce an elevation of thermal energy and food oxygenation induce lipid oxidation reactions (KANNER 1994; DONNELLY & ROBINSON 1995; RHEE 1988). Other factors, such as pH, aw, Eh, and food packaging procedures could also be associated with lipid oxidation in foods (CHEN & WAIMELEONGORA-EK 1981; TORRES et al. 1994; WANG et al. 1995).

Lipid oxidation of unsaturated fatty acids is initiated by the abstraction of hydrogen in carbon adjacent to the unsaturated bound. The reaction continues by the propagation step that is characterized by decomposition of unstable peroxides and finally results in the production of stable lipid oxidation products of the termination step (RHEE 1988; KANNER 1994; DONNELLY & ROBINSON 1995).

Supported by Grants from “Process de Amparo ao Pesquisa do Estado de São Paulo” – FAPESP (No. 944848-2/95-5757-2), and “Conselho Nacional de Desenvolvimento Científico e Tecnológico” – CNPQ.
Most of the toxic products are formed in the termination step. Aldehydes (malonaldehyde, hydroxynonenal, hydroxyhexenal), ketones, hydrocarbons, epoxides, alcohol, and other organic molecules are formed (PEARSON et al. 1983; ESTERBAUER et al. 1991; KUBOW 1992; FERRARI 1998a). The presence of these compounds in foods is associated with warmed-over flavour (TIMS & WATTS 1958; PEARSON et al. 1977) and other food sensory alterations (GREENE & CUMUZE 1981), in addition to their marked relations to the pathogenesis of cardiovascular diseases (especially atherosclerosis), diabetes, nutritional disorders, cancer and other pathologies (PEARSON et al. 1983; ESTERBAUER et al. 1991; KUBOW 1992; FERRARI 1998a, b, 1999, 2000).

The aim of this paper was to evaluate lipid oxidation (by the TBA test) and its possible correlation with food quality parameters (Eh, pH, and $a_w$) in sausages sold on City Hall Food Markets, known as “sacolões”, in the town of São Paulo, Brazil.

**MATERIALS AND METHODS**

**Samples**

During six consecutive weeks, six CHFMs marketing sausages were visited and thirty-six food samples were collected ($n = 36$). These methodology was important to verify that sausages were sold uninterruptedly, not only during that time period. Each sample weighing 250 g was collected in random by the food handler. With the exception of CHFM-6, which sold only poultry meat sausages, all CHFMs marketed Frankfurter sausages. It was not possible to assess the sausage producers because CHFM sellers can freely choose them, in view of low prices and availability (although the majority had chosen “Aurora’s” company). The geographic distribution of CHFMs is represented in Table 1 (FERRARI 1998b). All experiments described below were carried out in triplicates.

**2-thiobarbituric acid test (TBA-test)**

The TBA-test determines the contents of malonaldehyde (MDA), 1,3-dicarbonyl aldehyde ($C_3H_4O_2$) and other 2-thiobarbituric acid reactive substances (TBARS) in foods. In the reaction between two TBA acid molecules and one MDA molecule, a red pigment is formed and detected spectrophotometrically by absorption of 530–532 nm. The distillation method developed by TARLADGIS et al. (1964) was used with some modifications (KUBOW 1992; TORRES et al. 1994; TORRES & OKANI 1997). Briefly, 10 g of sample and 50 ml of distilled water are put in a beaker and homogenized by vortis for two minutes. The homogenate is transferred to a Kjeldahl flask. Subsequently, 47.5 ml of distilled water, 2.5 ml of HCl (4 mol/l), some anti-foaming drops, some glass beads, and 2 ml sulfanilamide solution (0.5% in 20% HCl solution) are added. The mixture is then distilled under intensive heating until 50 ml of distillate is collected in an Ernlemeyer flask. The flask is agitated. 5 ml aliquots are then withdrawn and transferred to test tubes to which 5 ml of 2-TBA solution (0.02 mol/l) are further added. The test tubes are closed and heated in a water bath at 96°C for 35 min. After cooling, absorbance at 532 nm is read using an UV-vis spectrophotometer (CE1020 model, Cecil – UK).

**Determination of redox potential (Eh) and pH**

Both Eh and pH were measured with a portable potentiometer containing KCl electrode that was calibrated at two points ($pH = 4.0$ and $pH = 7.0$) according to the book of instructions (FERRARI 1998b).

**Determination of water activity ($a_w$)**

$a_w$ was measured by an automatic analyzer equipment developed by Aqualab-Decagon Devices Inc., model CX-2 (Washington/USA). $a_w$ was expressed by the ratio of the pressure of food water vapour to the pure water vapour pressure (FERRARI 1998b).

**Planning and evaluation of experiments**

Parametric and non-parametric tests were used to evaluate the variables in the selected places and during the determined period of time. To evaluate possible correlations between the variables studied, SPSS 7.5.1 program for Windows was used.

**RESULTS**

**TBARS values of CHFM sausages (mg TBARS/kg sample)**

Table 2 presents the TBARS values of sausages marketed on CHFMs of the town of São Paulo. The mean of TBARS was $X \pm \sigma_w = 0.44 \pm 0.23$ mg TBARS/kg of sample. The values ranged from $0.38 \pm 0.19$ mg TBARS/kg (CHFM-6) to $0.58 \pm 0.31$ mg TBARS/kg (CHFM-2), with limits of 0.22 mg TBARS/kg and 1.08 mg TBARS/kg. The results of the analysis of variance and Kruskal-Wallis test (ANOVA) ($\chi^2 = 3.37; P = 0.6423$) did not reveal any statistically significant differences.
The results of Eh for CHFMs sausages are shown in Table 3. Eh mean was $X \pm \sigma_{n-l} = 39.03 \pm 26.30$ mV. The mean values of Eh ranged from $17.33 \pm 51.78$ mV (CHFM-3) to $56.67 \pm 25.70$ mV (CHFM-1) with extreme values of $-86.00$ to $92.00$ mV.

In the analysis of variance no statistically significant differences were observed. Kruskal-Wallis test did not reveal any statistically significant differences between the Eh means of six CHFMs ($\chi^2 = 3.14; P = 0.6785$).

The mean pH values ranged from $5.72 \pm 0.47$ (CHFM-1) to $6.13 \pm 0.21$ (CHFM-4), with the mean equal to $X \pm \sigma_{n-l} = 5.97 \pm 0.27$, with lower pH value 5.08 and higher pH value 6.48.

Kruskal-Wallis test resulted in a $\chi^2$ of 7.53, with $P = 0.1839$, revealing that there existed no statistically significant differences between the values of each CHFM. The same results were obtained by the analysis of variance.

**Water activity ($a_w$)**

Although $a_w$ ranged from 0.95 to 0.99 values $c \pm \sigma_{n-l} = 0.97 \pm 0.01$, there were no statistically significant differences in the analysis of variance (Table 5). The $\chi^2$ of Kruskall-Wallis was 6.98, with $P = 0.2219$.

**Statistical tests for possible correlations between quality parameters**

To verify possible correlations between the studied variables ($a_w$, pH, Eh, and TBARS values), three statistical tests were applied. Pearson’s correlation coefficient indicated a negative correlation between pH and Eh ($r = -0.50; P = 0.002$). No

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correlations between TBARS and the variables studied were found.

Spearman’s test also revealed a negative correlation of Eh and pH \((r = -0.7453; P < 0.05)\). In Kendall’s test the same result was obtained \((r = -0.6222; P < 0.05)\). These two tests failed to prove correlations between TBARS values and all the other quality parameters.

**DISCUSSION**

In the town of São Paulo, the city hall food markets (or sacolões) can represent an important source of foods for the population since the food price policy is very attractive to the consumers.

However, there are several risks associated with hygiene and the quality of sausages. Apart from some problems with local hygiene and poor handling, some sellers often wash sausages with water which can increase the risk of contamination (FERRARI 1998b). It was observed in a previous study that the moisture content and the storage temperature were totally inadequate thus increasing the risk of lipid oxidation and transmission of foodborne diseases to the population although the fat content was lower than that reported by other studies (FERRARI & TORRES 2000a, b).

Water activity values found by us were significantly higher than those reported by LEE and STYLIADIS (1996) who determined \(a_w\) values of 0.91 and 0.95 in dehydrated and fresh sausages, respectively.

The pH data found in CHFM sausages could allow the multiplication of several bacterial pathogens including *Clostridium botulinum* (LEITÃO 1988). The pH values

### Table 4. pH of sausages marketed on six City Hall Food Markets of São Paulo*

<table>
<thead>
<tr>
<th>Week</th>
<th>Locality</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5.43</td>
<td>5.94</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6.26</td>
<td>5.98</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>6.16</td>
<td>6.10</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>5.94</td>
<td>5.99</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5.47</td>
<td>5.95</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>5.08</td>
<td>6.20</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>5.72</td>
<td>6.02</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>0.46</td>
<td>0.10</td>
</tr>
</tbody>
</table>

CHFMs: 1 – Vila Maria Alta; 2 – Barra Funda; 3 – Rio Pequeno; 4 – João Moura; 5 – Bela Vista; 6 – Butantá

*The samples were analysed in triplicate

### Table 5. Water activity of sausages marketed on six City Hall Food Markets of São Paulo*

<table>
<thead>
<tr>
<th>Week</th>
<th>Locality</th>
<th>Mean</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

CHFMs: 1 – Vila Maria Alta; 2 – Barra Funda; 3 – Rio Pequeno; 4 – João Moura; 5 – Bela Vista; 6 – Butantá

*The samples were analysed in triplicate
obtained by us were lower than those reported by CARBALLO et al. (1991), who reported the mean of 6.2 ± 0.1. However, studying sausages marketed in Toronto, LEE and STYLIADIS (1996) determined pH means 6.2 for dehydrated, and 6.3 for fresh sausages, respectively. The statistical tests did not reveal any significant differences between CHFMs neither were any correlations found between pH and TBARS values, in contradiction to the study of CHEN and WAIMALEONGORA-EK (1981). In that paper the authors stated the lower is the pH, the higher is the lipid oxidation although that correlation was not statistically significant.

**Lipid oxidation measured by TBARS**

Lipid oxidation data did not show any statistically significant differences between the six CHFMs. However, the TBARS of sausages in this study were from 30% to 100% higher than the highest value (χ = 0.29) observed in sausages by REAGAN et al. (1983). On the other hand, the TBARS values were comparable to those reported by SHAMBERGER et al. (1977) who studied hot dog sausages; and also by AWORONIN (1993) who worked with smoked poultry sausages.

Recently, LORENZO et al. (2000) reported that sausages of the “Botilho” type presented an average TBARS value equal to 0.96 mg TBARS/kg and that sausages of “Androlla” type contained 4.05 mg TBARS/kg. In this study, the average TBARS values were lower than those reported by LORENZO et al. (2000).

On the other hand, literature data demonstrate that raw and cooked beef slices (PEARSON et al. 1977; NEWBURG & CONCON 1980), cuts of cooked poultry with skin or canned poultry sliced in cubes (PETERS et al. 1994), hamburgers (SHAMBERGER et al. 1977), and charqui (TORRES et al. 1989, 1994), a Brazilian traditional meat product, present higher TBARS values than those reported here. Lipid oxidation in charqui can be five to nine times higher than the values determined in this study (TORRES et al. 1989).

One of the most important quality parameters affected by lipid oxidation is the sensorial quality of foods (MORRISSEY et al. 1998). GREENE and CUMUZE (1981) observed that TBARS values higher than 0.6 mg/kg were really detected by persons making sensory analysis. According to this quality criteria (GREENE & CUMUZE 1981), 16.7% (6/36) of sausage samples could be considered to be of inadequate sensorial quality, and other 11.1% (4/36) presented critical TBARS values.

In a previous study with charqui (TORRES et al. 1994), a positive correlation was shown between a, and lipid oxidation that was not observed in this study.

Although the TBARS test does not measure MDA levels, it is important to note that chronic ingestion of lipid peroxidation products (MDA, 4-hydroxyxonenal, hexenals, peroxides, etc.) is associated with an increased risk of many chronic non-transmittable diseases (PEARSON et al. 1983; KUBOW 1992; DJURIC et al. 1998; FERRARI 1998a).


Meat products are rich sources of lipid oxidation products, and chronic high ingestion of these offers a considerable risk to the public health.

Two independent research groups observed that higher consumption of sausages increased the risk of childhood leukemia, brain tumors, lymphomas, and soft-tissue sarcomas in different populations of the United States (PETERS et al. 1994; SARASUA & SAVITZ 1994).

Studying the role of diet in DNA oxidation, DJURIC et al. (1998) found a positive correlation between the meat consumption and oxidative DNA damage to human blood cells. These authors also determined a negative correlation between the vegetable consumption and oxidative DNA injury.

Several in vitro, in vivo (animal) and epidemiological studies revealed that a high meat consumption and a lower fruit and vegetable intake, are associated with an increased risk of atherosclerosis and certain types of cancer, as recently reviewed (FERRARI 2001).

**Conclusions**

- The Eh values found in this study were sufficient for multiplication of microaerophilic bacteria;
- Elevated values of a, and pH were determined;
- With regard to the lipid oxidation, the TBARS values were intermediate;
- TBARS values of sausages marketed in CHFMs of São Paulo could be lower if high standards of quality during the production and storage were implemented and monitored by official authorities.

**References**


Received for publication June 19, 2001
Accepted after corrections February, 19, 2002

Abstrakt


Oxidace lipidů je jednou z nejvážnějších příčin zhoršování kvality potravin, zejména masných výrobků, a jsou s ní spojeny mnohé škodlivé vlivy na lidské zdraví. Během šesti týdnů jsme náhodně nakupovali vzorky potravin na městských potravinových tržištích (CHFMs) a zjišťovali jsme oxidaci lipidů (test TBARS) a některé ukazatele jakosti – redox potenciál (Eh), hodnotu pH a aktivitu vody (aw). Průměrná hodnota Eh činila X ± σn-1 = 39,03 ± 26,30 mV v rozmezí od –86,00 do 92,00 mV a průměrná hodnota pH X ± σn-1 = 5,97 ± 0,27 v rozmezí od 5,08 do 6,48. U jednotlivých vzorků jsme nezjistili statisticky významné rozdíly mezi hodnotami pH, Eh a aw. Průměrná hodnota testu TBARS činila X ± σn-1 = 0,44 ± 0,23 mg/kg v rozmezí od 0,38 ± 0,19 mg/kg (CHFM-6) do 0,58 ± 0,31 mg/kg (CHFM-2) s extrémním hodnotou 0,22 mg/kg a 1,08 mg/kg. Mezi hodnotami testu TBA a všemi testovanými ukazateli jsme nezjistili statisticky významné korelace. Podle kritérií senzorické analýzy (GREENE & CUMUZE 1981) 16,67 % vzorků párků by mělo být znehodnoceno a 11,11 % mělo kritické hodnoty TBARS.

Klíčová slova: oxidace lipidů; párky; maso; potravinové tržiště; ukazatelé jakosti

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